Rapport BIPM-2010/07

Bureau International des Poids et Mesures

Upgrade of the BIPM Standard Reference Photometers for Ozone and the effect on the on-going key comparison BIPM.QM-K1

by

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September 2010

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Abstract

The NIST Standard Reference Photometer (SRP) maintained by the BIPM and used as the reference in the international key comparison BIPM.QM-K1 was upgraded in March 2009. This followed the upgrade of almost all the other SRPs maintained by National Metrology Institutes or Designated Institutes which took part in this comparison. In order to ensure continuity between the comparisons performed before and after the upgrade, all degrees of equivalence between participants and the (upgraded) common reference have been recalculated and are presented in this report. The result is a very small shift of the common reference towards the centre of the distribution of participants. The good agreement with all participants has been maintained.

Contents:

1. Introduction

The reference method for the measurement of ground level ozone concentration is based on UV photometry, with the NIST SRP ozone reference standard acting as the primary standard for numerous national and international ozone monitoring networks. Several of these instruments are maintained by the BIPM, one of them being the reference standard for international comparisons of national ozone standards which have been coordinated by the BIPM[1] since 2003.

After the first international comparisons, which were performed in 2003-2005, the BIPM and the NIST undertook a study of systematic biases in the NIST SRP [1], which highlighted two major biases in the instrument. Before starting any further international comparisons, the BIPM decided to modify its SRPs in order to correct for the observed biases. One of the two biases, namely on the gas temperature evaluation, was removed with a physical modification of the instruments. For the second bias, arising from a limited knowledge of the light path length inside the instrument gas cells, a physical correction was not easy to achieve and a decision was made to numerically correct the path length of two SRPs (SRP27 and SRP28). A third BIPM instrument was physically modified and was used as internal reference to help monitor any drifts in the other SRPs.

Since then, the NIST developed an upgrade kit to physically remove the observed biases in the NIST SRPs, and started a series of upgrades of SRPs around the world [2]. The BIPM also performed some upgrades of other SRPs [3, 4]. National Metrology Institutes or Designated Institutes requested upgrades of their SRPs before taking part in the key comparison BIPM.QM-K1 cycle 1 (2007-2008) organized by the BIPM. The new comparison results clearly demonstrated that the measurement results of the common reference of the comparison, BIPM-SRP27 had slightly shifted from the mean of the group of upgraded SRPs. This shift was attributed to a difference between the numerical correction decided by the BIPM and the results of physical corrections introduced by the upgrade. These assumptions were confirmed by the more detailed study of the upgrade effect, which will be explained in a forthcoming paper.

In view of the above considerations, the BIPM, with the approval of the Gas Analysis Working Group of the CCQM, decided to undertake the upgrade of its two SRPs (27 and 28) after the completion of the first cycle of the key comparison BIPM.QM-K1 and before starting the second cycle (2009-2010). It was decided that all results from the first cycle of the key comparison would be recalculated to allow meaningful comparisons with following cycles.

This report presents the results of the upgrade of BIPM-SRP27 and BIPM-SRP28 and the effect on the key comparison BIPM.QM-K1. More details of the upgrade procedure and its effect on a number of SRPs in comparison with the study performed in 2005 will be published separately.

[1] http://www.bipm.org/en/scientific/chem/gas_metrology/ozone_comparisons.html

2. Brief description of the comparisons method

All comparisons reported here were performed by following the protocol of the key comparison BIPM.QM-K1, which can be downloaded from the BIPM website (http://www.bipm.org/utils/en/pdf/BIPM.QM-K1_protocol.pdf).

The results of one comparison between a participant and the BIPM, as published in the Key Comparison Database maintained by the BIPM, is a set of two degrees of equivalence. They are calculated at two nominal ozone mole fractions among the twelve measured in each comparison, in the range 0 nmol/mol to 500 nmol/mol: 80 nmol/mol and 420 nmol/mol. Degrees of equivalence before and after the upgrade of BIPM-SRP27 are presented in section 5 of this report.

In addition, comparisons can be meaningfully described by the two parameters of the linear regression performed between the measurement results of the two instruments involved, taking into account standard measurement uncertainties. To this end, a piece of software called OzonE was used. This software, which is documented in a publication [5], is an extension of the previously used software, B_Least, recommended by the ISO standard 6143:2001 [6]. It includes the possibility of taking into account correlations between measurements performed with the same instrument at different ozone mole fractions.

In a direct comparison, a linear relationship between the ozone mole fractions measured by SRP*n* and SRP27 is obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \qquad (1)$$

The associated uncertainties on the slope $u(a_1)$ and the intercept $u(a_0)$ are given by OzonE, as well as the covariance between them and the usual statistical parameters to validate the fitting function. Parameters of the linear regression for all participants before and after the upgrade of BIPM-SRP27 are presented in section 6 of this report.

3. Brief description of the BIPM SRPs

3.1. State of the BIPM SRPs before the upgrade

Compared to the original design described in [7], SRP27, SRP28 and SRP31 were modified to deal with two biases revealed by the study conducted by the BIPM and the NIST [1]:

- The three SRPs were equipped with a thermo-electric cooling device to remove excess heat from the lamp housing and to prevent heating of the cells. Together with a regular calibration of their temperature probe, this ensures the removal of the bias on the temperature measurement of the gas cell.
- In SRP27 and SRP28 the optical path length was calculated as being 1.005 times the total length of the two cells within each instrument. Together with an increased uncertainty, this takes into account the bias on the optical path length.

- In SRP31 the gas cells have been physically modified to avoid multiple reflections of the light beam on the end windows. The BIPM workshop designed new cell ends, in which the windows make a 3° angle with the vertical.

3.2. State of the BIPM SRPs after the upgrade

The SRP "upgrade kit" was installed in BIPM-SRP27 and BIPM-SRP28. The upgrade kit consisted of two parts:

- A new source block was designed to minimize the gas temperature evaluation bias by better thermal insulation of the UV source lamp (heated to a temperature of about 60 °C) from the rest of the optical bench, thus avoiding the temperature gradient observed in the SRP when the original source block was used.
- A new set of absorption cells were installed. The new cells consisted of quartz tubes closed at both ends by optically sealed quartz windows. These windows were angled at 3° to the vertical plane to avoid multiple reflections along the light path.

In addition, the thermo-cooling device designed at the BIPM was maintained in all three SRPs and was in-use during all comparisons.

3.3. Uncertainty budget of the BIPM-SRPs

The uncertainty budget for the ozone mole fraction in dry air x measured by the instruments BIPM-SRP27, BIPM-SRP28 and BIPM-SRP31 in the nominal range 0 nmol/mol to 500 nmol/mol is given in Table 1. The same uncertainty budget is applied to SRPs before and after the upgrade.

Table 1: Uncertainty budget for the SRPs maintained by the BIPM

Component (y)	**Uncertainty $u(y)$**				**Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$**	**Contribution to $u(x)$ $\lvert c_i \rvert \cdot u(y)$ nmol/mol**
	Source	**Distribution**	**Standard uncertainty**	**Combined standard uncertainty $u(y)$**		
Optical Path L_{opt}	Measurement Scale	Rectangular	0.0006 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89\times10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rect	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37\times10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
Temperature T	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29\times10^{-4}x$
	Temperature gradient	Rectangular	0.058 K			
Ratio of intensities D	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\ln(D)}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section α	Hearn value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-\frac{x}{\alpha}$	$1.06\times10^{-2}x$

Following this budget, the standard uncertainty associated with the ozone mole fraction measurement with the BIPM SRPs can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2} \qquad (2)$$

3.4. Covariance terms

As explained previously, correlations between the results of two measurements performed at two different ozone mole fractions with the BIPM maintained SRPs were taken into account in the software OzonE. More details on the covariance expression can be found in the protocol of the key comparison BIPM.QM-K1. The following expression was applied:

$$u(x_i, x_j) = x_i \times x_j \times u_\mathrm{b}^2 \qquad (3)$$

where:

$$u_\mathrm{b}^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_\mathrm{opt})}{L_\mathrm{opt}^2} \qquad (4)$$

The value of u_b is given by the expression of the measurement uncertainty: $u_\mathrm{b} = 2.92\times10^{-3}$ or $u_\mathrm{b}^2 = 8.5\times10^{-6}$.

4. Calculation of BIPM-SRP27 correction factors

All comparisons performed during the upgrade of SRP27 and SRP28 included SRP31 to monitor the changes in the measurement results. SRP31 was thus used as a transfer standard between SRP27 before the upgrade and SRP27 after the upgrade, in order to calculate correction factors for SRP27, as presented in this section.

Considering the relationship between SRP31 and SRP27 before the upgrade of SRP27:

$$x_\mathrm{SRP31} = a_0 + b_0 \cdot x_\mathrm{SRP27} \qquad (5)$$

Where the parameters of the linear equation take the following values:

b_0	$u(b_0)$	a_0 / (nmol/mol)	$u(a_0)$ / (nmol/mol)	$u(a_0, b_0)$ / (nmol/mol)
0.9974	0.0033	-0.19	0.21	-2.01×10^{-04}

And considering the relationship between SRP31 and SRP27 after the upgrade of SRP27 (the prime notation is used to indicate measurement results of SRP27 after its upgrade):

$$x_{\text{SRP31}} = a_1 + b_1 \cdot x'_{\text{SRP27}} \qquad (6)$$

Where the parameters of the linear equation take the following values:

b_1	$u(b_1)$	a_1 / (nmol/mol)	$u(a_1)$ / (nmol/mol)	$u(a_1, b_1)$ / (nmol/mol)
1.0008	0.0046	0.03	0.32	-5.08×10^{-04}

The relationship between SRP27 after the upgrade and SRP27 before the upgrade can be written:

$$x'_{\text{SRP27}} = a_2 + b_2 \cdot x_{\text{SRP27}} \qquad (7)$$

Where the parameters of the linear equation take the following values:

b_2	$u(b_2)$	a_2 / (nmol/mol)	$u(a_2)$ / (nmol/mol)	$u(a_2, b_2)$ / (nmol/mol)
0.9965	0.0056	-0.22	0.44	-4.57×10^{-06}

The correction parameters a_2 and b_2 are deduced from the equations:

$$b_2 = \frac{b_0}{b_1} \qquad (8)$$

$$a_2 = \frac{a_0 - a_1}{b_1} \qquad (9)$$

And their uncertainty from:

$$u(b_2) = b_2 \sqrt{\frac{u(b_1)^2}{b_1^{\,2}} + \frac{u(b_0)^2}{b_0^{\,2}}} \qquad (10)$$

$$u(a_2) = \frac{1}{b_1} \sqrt{u(a_0)^2 + u(a_1)^2 + (a_0 - a_1)^2 \frac{u(b_1)^2}{b_1^{\,2}}} \qquad (11)$$

$$u(b_2, a_2) = (a_0 - a_1) b_0 \frac{u(b_1)^2}{b_1^{\,4}} = a_2 b_2 \left(\frac{u(b_1)}{b_1} \right)^2 \qquad (12)$$

5. Recalculation of the degrees of equivalence

5.1. Definition

In the key comparison BIPM.QM-K1, degrees of equivalence for the participant i were calculated at two particular values: 80 nmol/mol and 420 nmol/mol, according to the following equation:

$$D_i = x_i - x_{\text{SRP27}} \tag{13}$$

where x_i and x_{SRP27} are the measurement result of the participant i and of SRP27 at the nominal value x_{nom}.

Its associated standard uncertainty is:

$$u(D_i) = \sqrt{u_i^2 + u_{\text{SRP27}}^2} \tag{14}$$

where u_i and u_{SRP27} are the measurement uncertainties of the participant i and of SRP27 respectively.

The correction factors a_2 and b_2 deduced from the comparison between SRP27 and SRP31 before and after the upgrade are used to calculate a corrected reference value and associated uncertainty:

$$x'_{\text{SRP27}} = a_2 + b_2 x_{\text{SRP27}} \tag{15}$$

$$u(x'_{\text{SRP27}}) = \sqrt{u(a_2)^2 + b_2{}^2 u(x_{\text{SRP27}})^2 + u(b_2)^2 x_{\text{SRP27}}{}^2 + 2x_{\text{SRP27}} u(a_2, b_2)} \tag{16}$$

In order to compute the corrected degrees of equivalence $D_\text{i}' = x_\text{i} - x'_{SRP27}$ and their associated uncertainties:

$$u(D'_\text{i}) = \sqrt{u_i^2 + u(x'_{\text{SRP27}})^2} \tag{17}$$

5.2. Particular case of the NMISA standard

The comparison performed between the NMISA and the BIPM is a particular case in BIPM.QM-K1, as the NMISA standard instrument was previously calibrated by the BIPM, just before performing the comparison. Therefore, measurement results of the NMISA and of the BIPM standards are correlated. Instead of equation 14, the uncertainty of the degree of equivalence D_i for the NMISA is written, as explained in [8]:

$$u(D_i) = \sqrt{u_i^2 - u_{\text{SRP27}}^2} \tag{18}$$

Similarly, measurement results of the NMISA and of the BIPM standards after the upgrade are correlated. Instead of equation 17, the uncertainty of the degree of equivalence for NMISA is written:

$$u(D_{\mathrm{i}}^{'}) = \sqrt{u_i^2 + u(x_{\mathrm{SRP27}}^{'})^2 - 2bb_2 \cdot u(x_{\mathrm{SRP27}}^{'})^2} \qquad (19)$$

Where b_2 is the slope of the correction to be applied to SRP27's measurement results, as defined in equation 8, and b is the slope of the linear relationship between the NMISA standard and SRP27: $x_i = x_{\mathrm{NMISA}} = a + bx_{\mathrm{SRP27}}$.

5.3. Values

The degrees of equivalence and their uncertainties calculated using the above equations are reported in Table 2 and Table 3 below. Corresponding graphs of equivalence are displayed in Figure 1. The expanded uncertainties are calculated with a coverage factor k = 2. All participants in the first cycle of BIPM.QM-K1 have been included, except the VSL for which results were not ready at the time this report was written. New degrees of equivalence for the VSL will be published later.

Table 2 : Degrees of equivalence of all participants in the key comparison BIPM.QM-K1 before and after upgrade of the reference BIPM-SRP27, at the nominal ozone mole fraction 80 nmol/mol.

Lab	date	x_{i}	$u(x_{\mathrm{i}})$	x_{ref}	$u(x_{\mathrm{ref}})$	x'_{ref}	$u(x'_{\mathrm{ref}})$	D'_{i}	$u(D'_{\mathrm{i}})$	$U(D'_{\mathrm{i}})$
NIST	Jan-07	76.30	0.43	76.34	0.52	75.85	0.80	0.45	0.91	1.83
NIST	Jan-07	76.50	0.44	76.54	0.52	76.05	0.81	0.45	0.92	1.83
ISCIII	Jun-07	83.95	0.60	84.56	0.38	84.05	0.75	-0.09	0.96	1.92
ISCIII	Jun-07	86.22	0.60	86.28	0.38	85.76	0.76	0.46	0.97	1.94
CHMI	Sep-07	80.34	0.37	80.47	0.37	79.97	0.73	0.37	0.81	1.63
INRIM	Sep-07	79.96	0.20	80.34	0.37	79.84	0.73	0.12	0.75	1.51
FMI	Oct-07	80.20	0.36	80.37	0.36	79.88	0.73	0.32	0.81	1.63
KRISS	Oct-07	82.13	0.65	80.23	0.37	79.74	0.73	2.39	0.98	1.96
UBA	Nov-07	78.31	0.44	78.58	0.53	78.09	0.82	0.21	0.93	1.86
VNIIM	Nov-07	79.76	0.31	80.04	0.29	79.54	0.69	0.22	0.76	1.52
VNIIM	Nov-07	81.13	0.32	81.36	0.29	80.86	0.70	0.28	0.77	1.53
NIM	Mar-08	71.12	0.42	71.53	0.51	71.06	0.78	0.06	0.89	1.77
LNE	Apr-08	80.79	0.37	81.14	0.35	80.64	0.72	0.15	0.81	1.62
NPL	May-08	79.62	0.28	80.21	0.37	79.71	0.73	-0.10	0.78	1.56
METAS	Jun-08	79.68	0.26	80.12	0.36	79.63	0.73	0.05	0.77	1.55
NMISA	Jul-08	80.00	1.30	80.76	0.37	80.27	0.73	-0.27	1.40	2.80
JRC	Dec-08	78.19	0.44	78.49	0.53	78.00	0.82	0.19	0.93	1.85
NPLI	Mar-09	79.68	0.44	79.90	0.54	79.41	0.82	0.27	0.94	1.87

Table 3 : Degrees of equivalence of all participants in the key comparison BIPM.QM-K1 before and after upgrade of the reference BIPM-SRP27, at the nominal ozone mole fraction 420 nmol/mol.

Lab	**date**	x_i	$u(x_i)$	x_{ref}	$u(x_{ref})$	x'_{ref}	$u(x'_{ref})$	D'_i	$u(D'_i)$	$U(D'_i)$
NIST	Jan-07	432.00	1.72	432.61	2.24	430.89	3.33	1.11	3.75	7.50
NIST	Jan-07	436.50	1.74	436.92	2.27	435.19	3.36	1.31	3.79	7.57
ISCIII	Jun-07	418.06	1.64	420.70	1.45	419.02	2.80	-0.97	3.25	6.50
ISCIII	Jun-07	422.92	1.66	423.66	1.46	421.98	2.82	0.94	3.28	6.55
CHMI	Sep-07	418.00	1.25	418.44	1.25	416.77	2.70	1.22	2.97	5.94
INRIM	Sep-07	419.13	0.56	420.85	1.26	419.17	2.71	-0.04	2.77	5.53
FMI	Oct-07	418.92	1.26	420.49	1.26	418.81	2.71	0.11	2.99	5.97
KRISS	Oct-07	422.03	2.09	419.54	1.26	417.87	2.70	4.16	3.42	6.84
UBA	Nov-07	419.70	1.68	420.62	2.18	418.95	3.24	0.76	3.65	7.29
VNIIM	Nov-07	410.70	1.22	412.17	1.25	410.52	2.66	0.18	2.93	5.86
VNIIM	Nov-07	419.70	1.25	421.52	1.28	419.84	2.72	-0.14	2.99	5.99
NIM	Mar-08	415.52	1.66	417.38	2.17	415.71	3.21	-0.19	3.62	7.24
LNE	Apr-08	420.51	1.26	422.31	1.29	420.62	2.73	-0.12	3.01	6.01
NPL	May-08	417.75	1.27	419.26	1.26	417.58	2.70	0.17	2.98	5.97
METAS	Jun-08	418.15	0.63	420.03	1.26	418.35	2.71	-0.21	2.78	5.56
NMISA	Jul-08	419.61	1.64	420.86	1.26	419.18	2.71	0.44	2.62	5.24
JRC	Dec-08	409.51	1.64	410.63	2.13	408.98	3.16	0.52	3.56	7.12
NPLI	Mar-09	399.50	1.60	401.12	2.08	399.51	3.09	-0.01	3.48	6.96

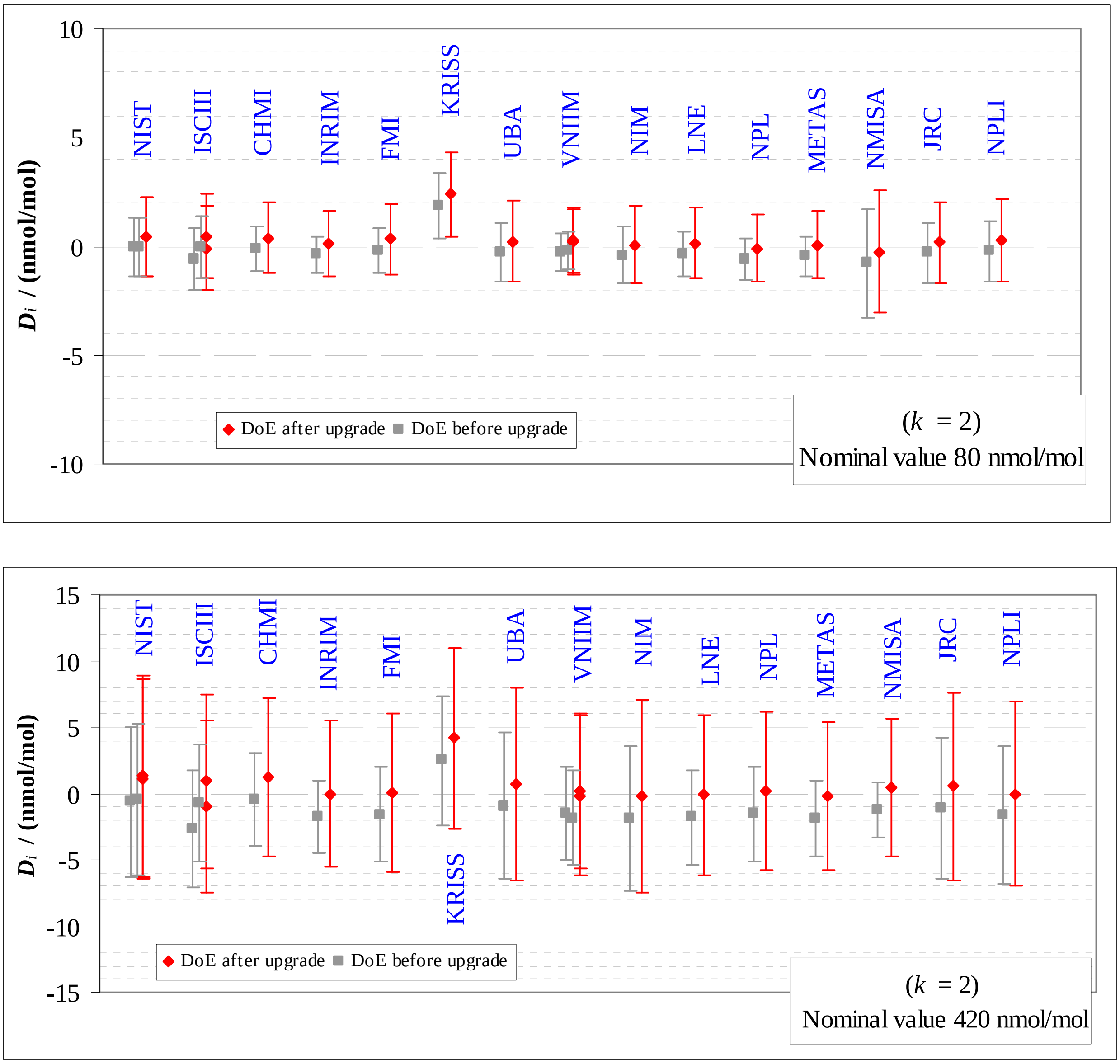


Figure 1: Graphs of equivalence of all participants in the key comparison BIPM.QM-K1 before and after upgrade of the reference BIPM-SRP27, at the nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol.

5.4. Analysis

The first important observation is that the upgrade of BIPM-SRP27 did not change the good agreement between all participants. All degrees of equivalence shifted only by a very small amount compared to the stated uncertainties. The average and the median values of the degrees of equivalence before and after the upgrade are displayed in Table 4:

Table 4: Average of the degrees of equivalence of all participants in BIPM.QM-K1 before and after the upgrade of BIM-SRP27

	before	**after**	before	**after**
nominal value / (nmol/mol)	80		420	
Average D_i / (nmol/mol)	-0.20	**0.31**	-1.10	**0.51**
median	-0.28	**0.21**	-1.49	**0.17**

Secondly, following the upgrade measurement, results from BIPM-SRP27 are indeed now closer to the centre of the distribution of participants' measurement results in the key comparison BIPM.QM-K1.

The uncertainties of all degrees of equivalence have slightly increased, due to the use of a transfer standard (SRP31) between SRP27 before and after the upgrade. The effect on the key comparison is however minor.

6. Recalculation of the least-square regression parameters

As explained in section 2, the parameters of the linear regression between two photometers' measurement results also constitute meaningful characteristics of the agreement between them. Therefore, those parameters which are always given for information in the key comparison BIPM.QM-K1 reports, were also recalculated, as well as their uncertainties, according to the following equation.

Considering the relationship between a photometer *i* and SRP27 before the upgrade of SRP27:

$$x_i = a + b \cdot x_{\text{SRP27}} \tag{20}$$

And the relationship between a photometer *i* and SRP27 after the upgrade of SRP27:

$$x_i = a' + b' \cdot x'_{\text{SRP27}} \tag{21}$$

Where the parameters *a'* and *b'* and their uncertainties are deduced from:

$$a' = a - \frac{a_2 b}{b_2} \tag{22}$$

$$b' = \frac{b}{b_2} \tag{23}$$

$$u(a') = \sqrt{u(a)^2 + \frac{b^2}{b_2^{\,2}} u(a_2)^2 + \frac{a_2^{\,2}}{b_2^{\,2}} u(b)^2 + \frac{(a_2 b)^2}{b_2^{\,4}} u(b_2)^2 - 2\frac{b^2 a_2}{b_2^{\,3}} u(a_2, b_2)} \tag{24}$$

$$u(b') = b' \sqrt{\frac{u(b)^2}{b^2} + \frac{u(b_2)^2}{b_2^{\,2}}} \tag{25}$$

<u>Particular case of the NMISA comparison:</u>

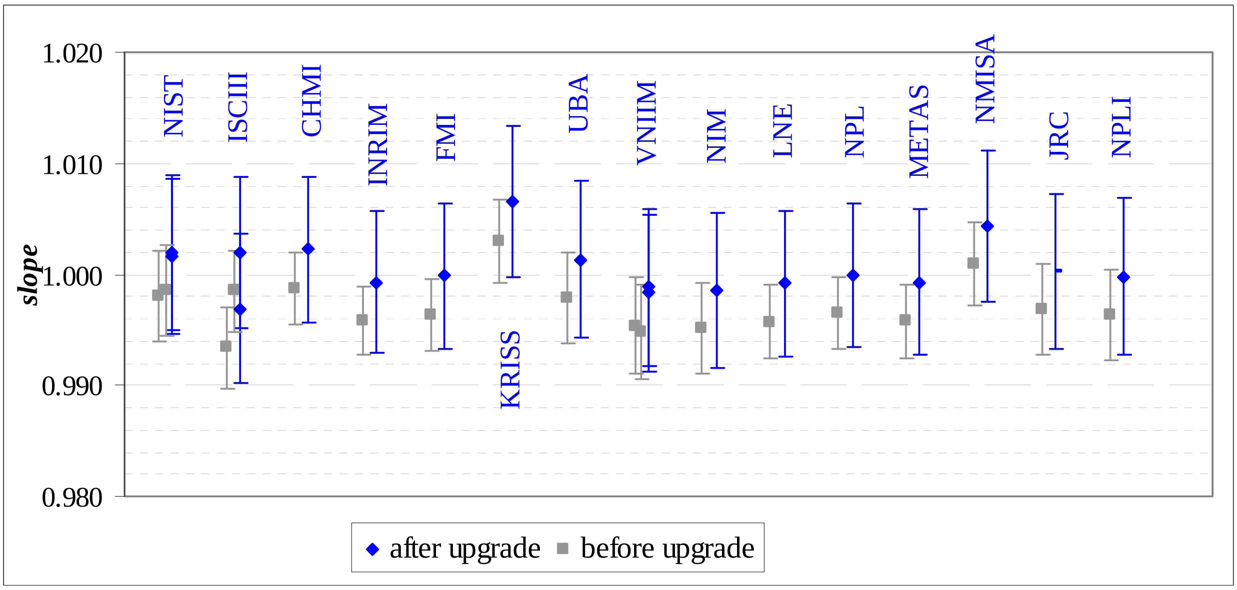
As discussed previously, covariance terms between the values associated with each instrument at the same nominal mole fraction should be calculated and taken into account when performing the regression. Unfortunately, this feature is not available in the software OzonE. As the least-square results are given in comparison reports for information only, the NMISA parameters were calculated without these covariances.

6.1. Values

The new parameters and their uncertainties, calculated using the above equations, are reported in Table 5. The corresponding graphs are displayed in Figure 2. The expanded uncertainties are calculated with a coverage factor $k = 2$.

Table 5 : New parameters of the linear regression between each participant standard and the common reference standard SRP27 after its upgrade.

Lab	date	b'	$u(b')$	a'	$u(a')$
NIST	Jan-07	1.0016	0.0070	0.29	0.55
NIST	Jan-07	1.0020	0.0070	0.28	0.55
ISCIII	Jun-07	0.9969	0.0067	0.23	0.56
ISCIII	Jun-07	1.0020	0.0067	0.18	0.56
CHMI	Sep-07	1.0022	0.0065	0.21	0.49
INRIM	Sep-07	0.9993	0.0064	0.25	0.47
FMI	Oct-07	0.9999	0.0065	0.17	0.49
KRISS	Oct-07	1.0065	0.0068	0.47	0.55
UBA	Nov-07	1.0014	0.0070	0.22	0.55
VNIIM	Nov-07	0.9989	0.0071	0.42	0.49
VNIIM	Nov-07	0.9983	0.0071	0.40	0.49
NIM	Mar-08	0.9986	0.0070	0.24	0.55
LNE	Apr-08	0.9992	0.0065	0.17	0.51
NPL	May-08	1.0000	0.0065	0.21	0.47
METAS	Jun-08	0.9993	0.0065	0.13	0.48
NMISA	Jul-08	1.0044	0.0068	-0.59	0.56
JRC	Dec-08	1.0003	0.0070	0.21	0.55
NPLI	Mar-09	0.9998	0.0070	0.15	0.55



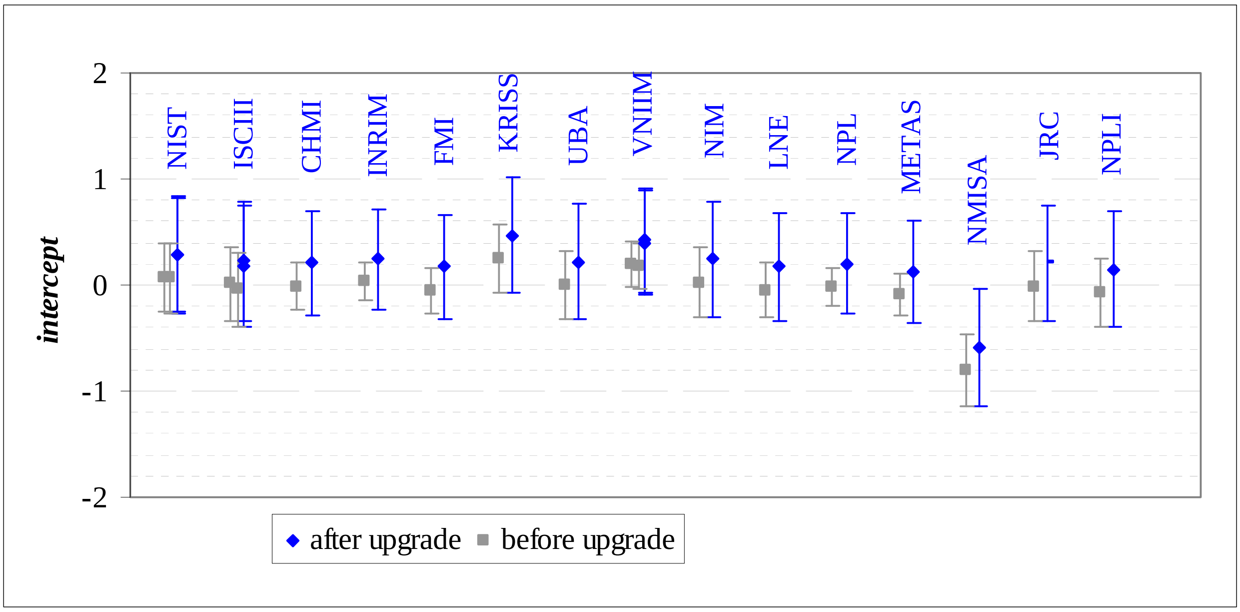


Figure 2: Parameters of the linear regression between each participant standard and the common reference standard SRP27 for all participants in the key comparison BIPM.QM-K1 before and after upgrade of the reference BIPM-SRP27.

6.2. Analysis

As with the degrees of equivalence, the first important observation is that the upgrade of BIPM-SRP27 did not change the good agreement with all participants. All slopes have shifted by a very small amount compared to their stated uncertainties. The average and the median of the degrees of equivalence before and after the upgrade are given in Table 6:

Table 6: Average and median of the regression parameters of all participants in BIPM.QM-K1 before and after the upgrade of BIM-SRP27

	before	**after**	before	**after**
	Slope		Intercept / (nmol/mol)	
Average	0.9972	**1.0006**	-0.01	**0.20**
Median	0.9964	**0.9999**	0.01	**0.21**

It appears that the measurement results from BIPM-SRP27 are now closer to the centre of the distribution of participants' measurement results in the key comparison BIPM.QM-K1.

7. Conclusion

The NIST SRP, maintained by the BIPM and used as the reference in the international key comparison BIPM.QM-K1, underwent an upgrade in March 2009. This followed the upgrade of almost all the other SRPs maintained by National Metrology Institutes or Designated Institutes. In order to ensure the continuity between comparisons performed before and after the upgrade, all degrees of equivalence between participants and the (upgraded) common reference have been recalculated. As expected, the effect of the upgrade on comparison results was a minor shift of the common reference BIPM-SRP27 towards the centre of the distribution of results. This was expected, based on the origin of the remaining difference between BIPM-SRP27 and other upgraded SRPs, which was a numerical correction of the bias on the light path length compared to a physical correction, as will be explained in a forthcoming publication on SRP upgrades.

8. References

[1] Viallon J., Moussay P., Norris J.E., Guenther F.R. and Wielgosz R.I., 2006, A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer. *Metrologia* **43** 441-450

[2] Norris J.E., Viallon J., Moussay P., Guenther F.R. and Wielgosz R.I., 2008, Results of Temperature Gradient and Path-length Bias Modifications to NIST Ozone Reference Standards. In: *Air & Waste Management 101st Annual Conference*, (Portland, Oregon)

[3] Viallon J., Moussay P., Wielgosz R., Walden J. and Kuronen P., 2009, Final report, on-going key comparison BIPM.QM-K1: Ozone at ambient level, comparison with FMI, 2007. *Metrologia* **46** 08009

[4] Viallon J., Moussay P., Wielgosz R.I., Quincey P. and Sweeney B., 2009, Final report, on-going key comparison BIPM.QM-K1: Ozone at ambient level, comparison with NPL, 2008. *Metrologia* **46** 08011

[5] Bremser W., Viallon J. and Wielgosz R.I., 2007, Influence of correlation on the assessment of measurement result compatibility over a dynamic range. *Metrologia* **44** 495-504

[6] ISO 6143.2 : 2001 Gas analysis - Determination of the composition of calibration gas mixtures - Comparison methods (International Organization for Standardization)

[7] Paur R.J., Bass A.M., Norris J.E. and Buckley T.J., 2003, Standard Reference Photometer for the Assay of Ozone in calibration Atmospheres. *NISTIR* **6963** (NIST)

[8] Viallon J., Botha A., Wielgosz R.I. and Moussay P., 2010, Final report on the on-going key comparison BIPM.QM-K1: Ozone at ambient level, comparison with NMISA, 2008. *Metrologia* **47** 08014